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ENVIRONMENT-SENSITIVE HARDNESS AND
MACHINABILITY OF ALUMINA

Albert R. C. Westwood, et al

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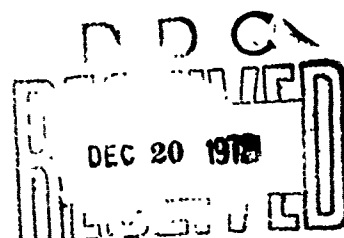Corporate Research and
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13. ABSTRACT

The influences of water, toluene and the n-alcohols on the pendulum hardness of alumina monocrystals, and on the ease of drilling mono- and polycrystalline alumina, have been studied. It has been found that the adsorption-induced increases in pendulum hardness produced by certain alcohol environments can result in rates of drilling with diamond-studded core bits which are up to ten times greater than those measured in tests under water. A correlation between pendulum hardness, machinability and surface charge (the latter as indicated by ζ-potential measurements) has been established. This is that alumina is hardest and most effectively drilled with a diamond core bit at its zero point of charge. The possibility of making use of this correlation to develop more cost effective and ecologically viable cutting fluids for the machining of alumina is discussed.

Details of illustrations in
this document may be better
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I. Introduction

A high degree of surface perfection is extremely important to the successful use of alumina ceramics as epitaxial substrates for microelectronic applications. Because of this, machining costs can sometimes represent as much as 60 - 90% of the total cost of a component.[1] Surface quality also plays a major role in determining the mechanical reliability of substantially larger structural components made from alumina. Clearly, therefore, a more economical way of producing surface finishes of reproducibly high quality on this extremely hard material would be of technological value. Such might be achieved by controlled, adsorption-induced variations in near-surface hardness -- i.e., by utilization of chemomechanical effects such as the Rebinder effect.[2] Recent studies by Westwood et al.[3-5] have demonstrated that chemomechanical effects in crystalline non-metals are caused not by adsorption-induced reductions in the surface free energy, as first thought[2], but rather by adsorption-dependent variations in the mobility of near-surface dislocations. In MgO and CaF_2, for example, a direct correlation has been demonstrated between the influence of a given chemical environment on near-surface dislocation mobility and on the ease with which these solids may be drilled with a carbide spade bit.[6]

According to present understanding,[7,8] surface active environments might be expected to influence the machining behavior of alumina if (i) dislocations in alumina are sufficiently mobile at or near room temperature to provide some plastic flow in a rear-surface layer

$\sim 1 - 10$ μm deep, (ii) mobile dislocations play any significant role in determining the fracture behavior of alumina at these temperatures, and (iii) the mobility of near-surface dislocations in alumina can be significantly influenced by the adsorption of surface-active species.

A survey of the literature suggests that at least two of these criteria can be met. First, there is increasing evidence for limited dislocation mobility in alumina at room temperature. For example, the measured fracture energy of alumina (6 - 40 J/m^2)[9,10] is many times greater than its equilibrium surface energy (estimated by several methods as ~ 1 J/m^2)[11,12], suggesting that fracture is not completely brittle. The temperature dependence of the fracture energy[13] also is much larger than the likely variation with temperature of either the elastic constants or the equilibrium surface energy, and this too is consistent with the occurrence of plastic flow during fracture. Furthermore, high dislocation densities, and also twins, have been detected in flakes taken from fracture surfaces and examined by electron microscopy[13], and X-ray evidence of plastic deformation near fracture surfaces has also been obtained[14]. Dislocations have also been detected in explosively shocked alumina[15], and around indentations and scratches made on several crystallographic surfaces at room temperature[16]. Of course, during indentation and abrasion, and also under shock loading conditions, there is a significant component of hydrostatic stress present during deformation which is likely to enhance the occurrence of plastic flow.

Second, there is evidence that the adsorption of surface active species can significantly influence the near-surface electrical properties of sapphire. For example, adsorbed oxygen can increase near-surface conductivity 10^2 - 10^3 times, and the effective thickness of the conducting charge double layer has been estimated to be $\sim 10 \ \mu m$[17]. Similar changes in conductivity occur also in MgO[17] - a material which exhibits marked chemomechanical phenomena[3,4]. Thus, if adsorption-induced changes in the concentration or mobility of charge carriers can influence near-surface dislocation mobility in alumina in much the same manner as they are considered to do in MgO[3,4,8], then environmentally-induced changes in the near-surface hardness of alumina may be expected. Indeed, one example of such behavior has already been observed, namely anomalous indentation creep associated with adsorbed water[18].

However, whether dislocations in alumina are intrinsically sufficiently mobile, or can be induced to be sufficiently mobile by environmental effects, to influence room temperature <u>fracture</u> behavior[*] to any significant degree is the critical issue in determining whether or not application of the chemomechanical effects to the machining of alumina is likely to be a practical possibility.

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[*]Observations of delayed failure in alumina[19] lead us to suggest[20] that the ease with which slowly propagating, sub-critical cracks extend can be influenced by adsorbed species -- possibly as a consequence of environment-dependent flow behavior in the vicinity of the crack tip.

This paper presents the first results of an investigation undertaken in order to resolve this issue. Our efforts so far have been focused on establishing the existence and evaluating the potential significance of chemomechanical effects in the machining of alumina, rather than on mechanistic aspects.

II. Experimental

(1) Materials

Alumina monocrystal slabs, approx. 25 mm across and 6mm thick, were cut from a large boule grown by the Czochralski technique[*]. They contained only a few parts in 10^5 of impurities, and a grown-in dislocation density of 10^4 - $10^5/cm^2$. Some specimens were cut with their major planes parallel to $\{0001\}$, and others with these faces parallel to $\{1\bar{1}02\}$ (as identified by the etching technique developed by Vardiman[21]). Polycrystalline specimens were prepared from Lucalox[**] and from material provided by the Avco Corporation[‡]. These were of greater than 99.9% theoretical density and purity. The grain size of the Lucalox was 20 - 40 μm and that of the Avco alumina 5 - 10 μm. The environments used were water-free toluene, water, aqueous solutions of sodium hydroxide, pure n-alcohols and binary solutions of these.

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[*] Purchased from the Crystal Products Division of Union Carbide, San Diego, California.

[**] A product of the General Electric Company.

[‡] Courtesy of Dr. T. Vasilos, Avco Corporation.

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(2) Test Procedures

Three experimental procedures were used to assess the influence of chemical environment on near-surface mechanical behavior.

(a) Microindentation Measurements - Knoop and Vickers indentation tests were performed on monocrystal surfaces cut parallel to $\{1\bar{1}02\}$ and polished either mechanically using 0.25 μm diamond paste or chemically in orthophosphoric acid at 400 - 420°C. Indenter loads were in the range 25 - 200g.

(b) Pendulum Hardness Measurements - Measurements of the rate of damping of a pendulum sclerometer[22] were made on $\{1\bar{1}02\}$ or $\{0001\}$ monocrystal surfaces produced under the appropriate test environment either by abrasion on a diamond wheel or by fracture. The fractured surfaces were prepared by cutting a groove half-way through a rectangular slab, and then striking sharply at the base of this groove with a steel chisel. This produced approximately flat surfaces roughly parallel to the plane of the groove. Note, however, that these are not cleavage surfaces in the strict crystallographic sense.

The pendulum used in the present work is shown in Fig. 1. It consists of a long pointer and a diamond fulcrum (either a 70° cone or a 136° pyramid) mounted respectively above and below the midpoint of a horizontal beam. The pendulum is stabilized by equal weights rigidly suspended below the ends of the beam. When not in use the
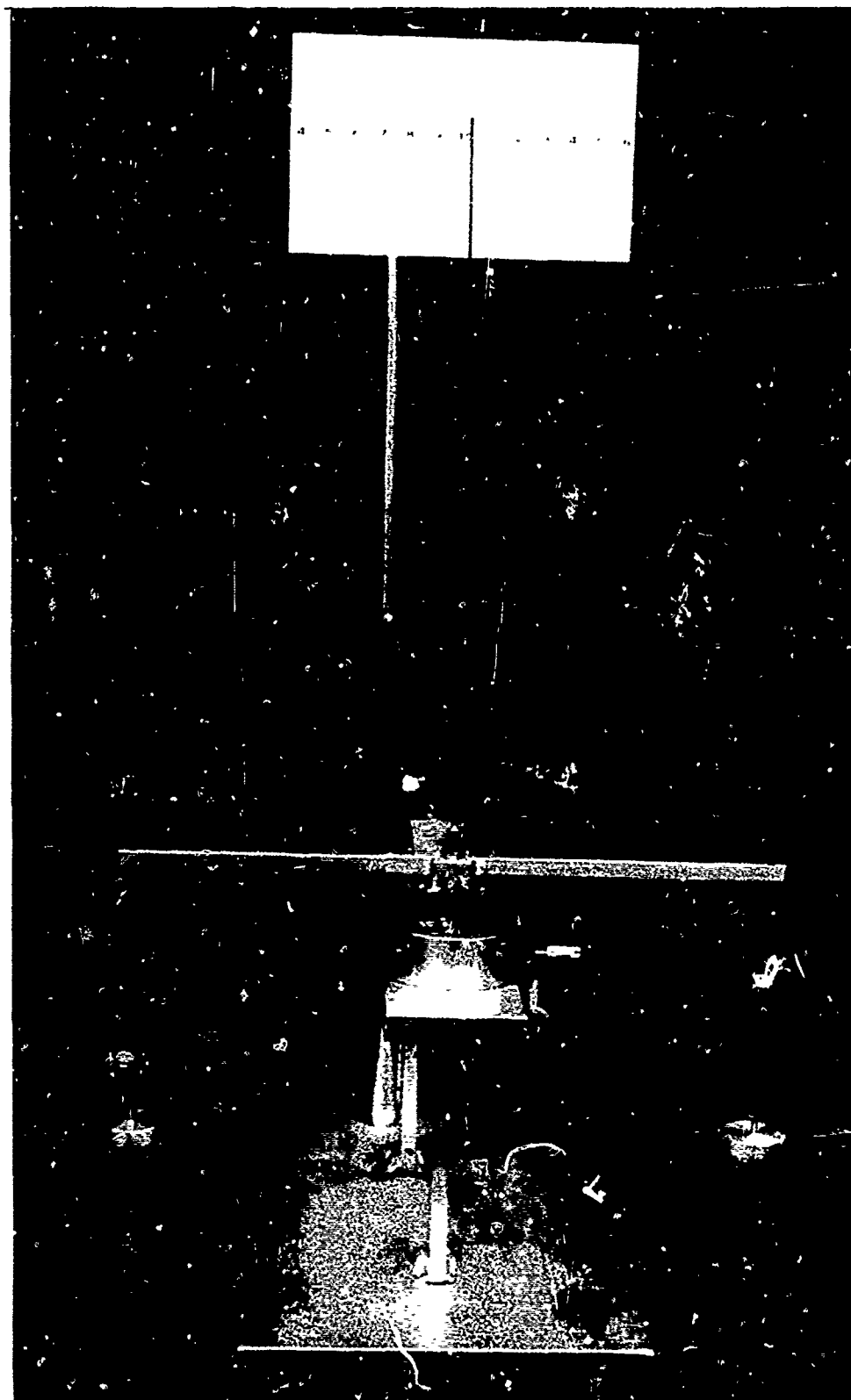
Fig. 1   -   Pendulum Hardness Apparatus

pendulum is supported by a yoke straddling the fulcrum beneath the center of the horizontal beam and attached to a support stand. This yoke can be lowered by a lever and eccentric cam arrangement, leaving the fulcrum resting on the specimen surface and the pendulum free to swing. The total pendulum weight is 140 g, and its period of oscillation ~1 s. The specimen is clamped in a shallow holder filled to a constant depth with the chosen test environment.

In operation, the pendulum and support stand are enclosed in a box to minimize the effects of air currents, and the pendulum is set oscillating with a fixed initial amplitude, A(0). A travelling microscope focussed on the pendulum pointer and the centimeter scale at the top of the stand is used to record the amplitude, A(t), after time t. Pendulum hardness, H, is calculated from the relationship[23]

$$H = t/2.303 \, (\log A(0) - \log A(t)).$$

In the present work t was 300 s. H is thus an arbitrary measure of the rate of pendulum damping, and is related to the energy absorbed by near-surface flow and fracture processes occurring beneath the fulcrum. For a hard and brittle solid relatively little energy is absorbed, and H is large. For a softer and more ductile solid more energy is absorbed, the rate of damping is increased, and the magnitude of H is correspondingly less.

Figure 3 shows the extent of damage produced by the rocking pendulum on an abraded $\{1\bar{1}02\}$ surface in (moist) air.
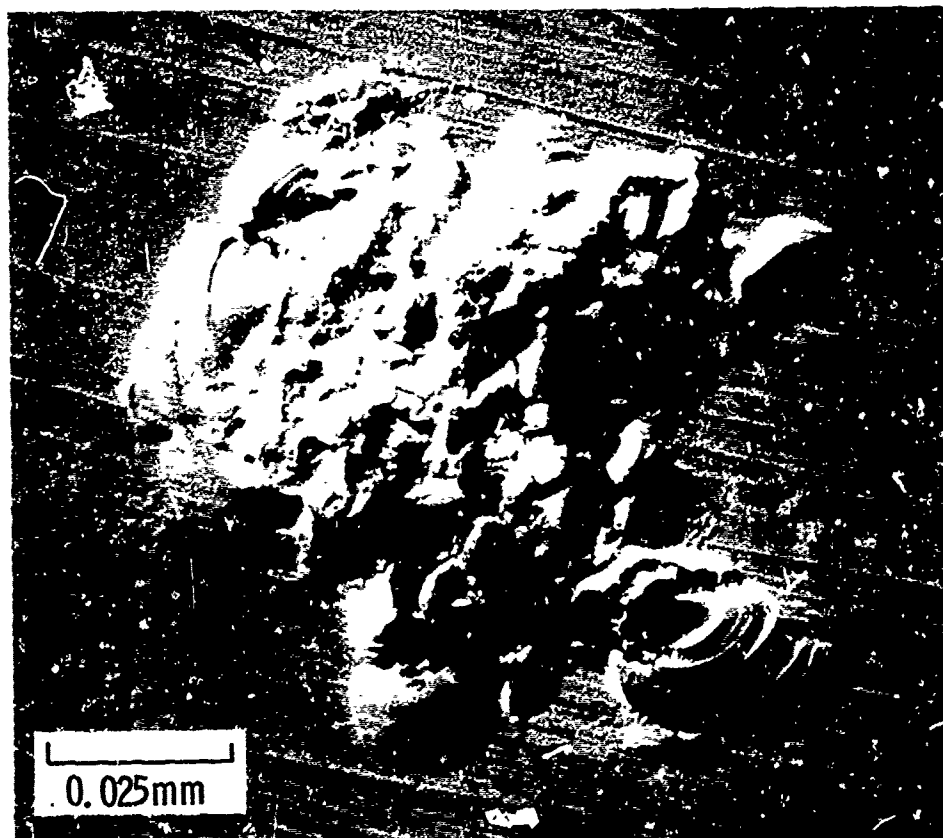
Fig. 2 - Damage produced on abraded {1̄102} alumina
surface by pendulum sclerometer. 300 s in moist air
environment.

(c) Drilling Studies - Mono- and polycrystalline alumina specimens were drilled in various liquid environments using a precision drill press and 3.2 mm o.d. diamond-loaded core bits. ·The wall thickness of these bits was ~ 1 mm. A fixed load, typically 5 kg, was applied to the bit by means of a lever, and penetration was recorded by means of an LVDT system. Bit rotation speed was 2200 r.p.m. throughout. Monocrystal specimens were drilled normal to either $\{0001\}$ or $\{1\bar{1}02\}$ surfaces.

III. Results

(1) Microindentation Experiments

Although the Knoop and Vickers microhardness values determined in this work were within the range of values published by other investigators (1250 - 3100 kg/mm^2), because of excessive scatter it was not possible to draw from them any meaningful conclusions about the effects of environment on hardness. The principal cause of this scatter was the difficulty of measuring accurately and reproducibly the small indentations necessary to reveal any environment-sensitivity of hardness in alumina. Westbrook and Jorgensen [18] have shown, for example, that the ratio of the Vickers hardness of alumina in (moist) air to that in toluene varies from ~0.80 for a 25g load applied for 15 s to ~0.95 for a 75g load applied for the same time. For loads of 100g or more the ratio is 1.00, and hardness then is relatively insensitive to any change in environment. However, the dimensions of a Knoop microhardness indentation produced in alumina using an

applied load of 25g are only ~10-14 μm long, ~1.5-2 μm wide and ~0.4 - 0.5 μm deep. Also, the difference in size of the maximum dimension of indentations made in the presence and absence of an active environment, assuming an intrinsic hardness of 2000 kg/mm^2 and an environmentally-induced reduction in hardness of 20%, is only ~1.5 μm, which is close to the ~0.5-1 μm limit of resolution of an optical microscope under optimum conditions. Hence, bearing in mind the shallow nature of such indentations and the consequent lack of contrast, reproducibility problems are only to be expected.

(2) Pendulum Hardness Measurements

Figures 3 (b) and 4 (b) present the variation in pendulum hardness of alumina monocrystals in aqueous sodium hydroxide solutions and in the n-alcohols respectively. N_C is the number of carbon atoms in the alcohol molecule. Now, previous work has established the existence of a simple relationship between surface charge (as indicated by ζ-potential) and pendulum hardness for soda-lime glass[20] and quartz[8] - namely that these solids are hardest at their zero points of charge (z.p.c.). Hence, the possibility that such a relationship might also exist for alumina was of particular interest. For purposes of comparison, therefore, Figs. 3 (a) and 4 (a) present ζ-potential versus environmental composition data for alumina in aqueous sodium hydroxide solutions (after Modi and Fuerstenau[24]) and in the n-alcohols (after Gortner[25]). Note that a maximum in pendulum hardness occurred when the specimens were immersed in ~10^{-5} molar sodium hydroxide and in pentyl alcohol. Thus, in both of these cases it would appear that alumina, like quartz, is hardest when its surface charge is approximately zero - i.e., when $\zeta \simeq 0$.
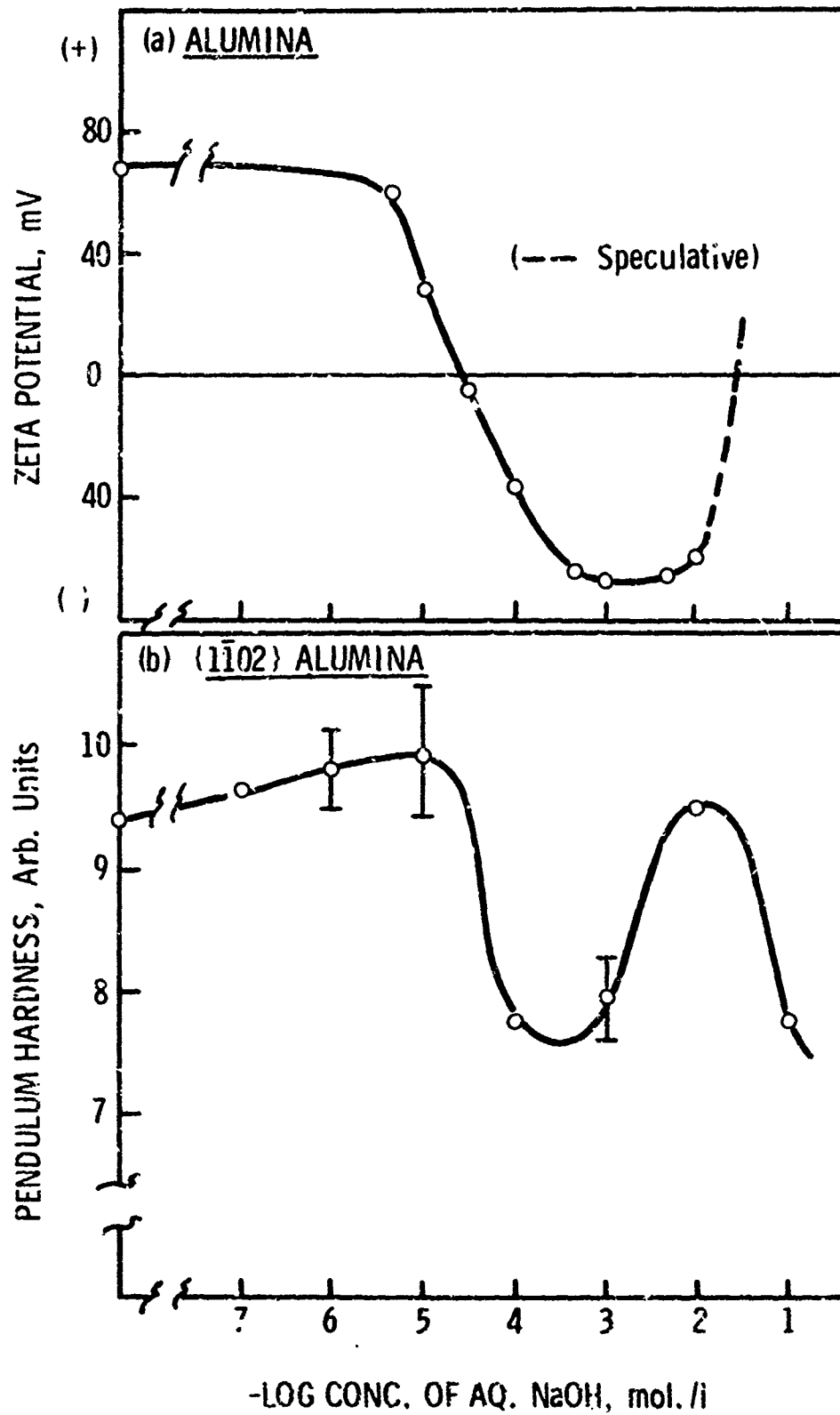
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Fig. 3 - (a) Zeta potential[24] and (b) pendulum hardness of alumina in aqueous sodium hydroxide solutions.
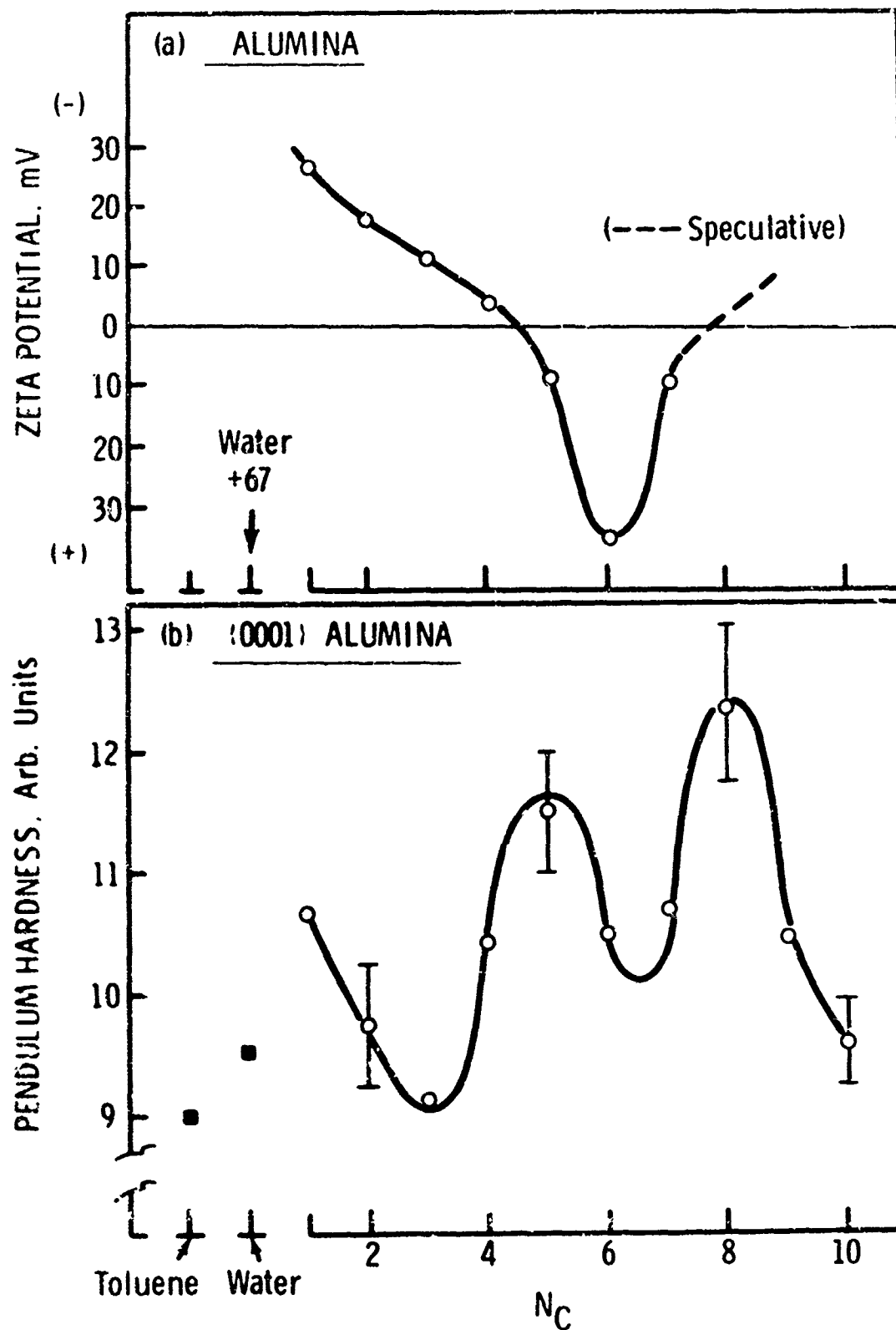
Fig. 4 - (a) Zeta potential[25] and (b) pendulum hardness of alumina in the n-alcohols, toluene and water.

The pendulum hardness maxima observed in $\sim 10^{-2}$ molar sodium hydroxide and octyl alcohol environments could also be related to the occurrence of zero surface charge on the alumina if our hypothetical extrapolations of the established ζ-potential data presented in Figs. 3 (a) and 4 (a) are valid.   Preliminary data from experiments by D. H. Taylor in our laboratory utilizing the streaming potential technique   suggest   that   in   the   case   of   the   alcohol environments our extrapolation may be correct.   However,   both in solutions of relatively high ionic concentrations (such as 10^{-2} molar sodium hydroxide), and in environments of very low conductivity (such as the higher alcohols), data obtained using the streaming potential technique are questionable because certain fundamental assumptions underlying the analysis used to derive the ζ-potential become untenable[26].

It will be noted from Fig. 4 (a) that the   surface of alumina is positively charged in water, but negatively charged in methyl alcohol.   Thus, adding increasing amounts of water to methyl alcohol might be expected to first increase   the ζ-potential of alumina to zero, and then to reverse its charge.   On the basis of the results presented in Fig.   4,   one would anticipate therefore the occurrence of a maximum in the pendulum hardness of alumina in that particular methyl alcohol-water solution which produces zero surface charge on the solid. Streaming potential measurements by Taylor have revealed that alumina does indeed exhibit a z. p. c. in a methyl alcohol-water solution containing < 5v/o of water. while pendulum hardness experiments have demonstrated the occurrence of the predicted maximum in hardness in methyl alcohol - 3 v/o water solutions.

(3) Drilling Experiments

Figure 5 presents bit penetration rate data for mono-crystal alumina specimens drilled normal to $\{1\bar{1}02\}$ while immersed in the n-alcohols. $\dot{D}(200)$ is the average penetration rate during the interval from 150 to 250 s after drilling is commenced. Especially interesting is the observation that the variation of $\dot{D}(200)$ with N_C exhibits the same characteristic double maximum seen in the pendulum hardness data of Fig. 4 (b). Of more practical significance, however, is the fact that, under the experimental conditions employed, alumina may be drilled some ten times faster in octyl alcohol than in water.

To establish that the variations of $\dot{D}(200)$ with N_C are unlikely to be related to any corrosive influences of the environment, to lubricating or cooling phenomena, or to the presence of impurities in the n-alcohols, similar measurements were made using binary solutions of the n-alcohols. In these experiments bit penetration was measured perpendicular to $\{0001\}$ planes, rather than $\{1\bar{1}02\}$ planes, and exact matching of the values of $\dot{D}(200)$ for the pure alcohols was not observed. The data presented in Fig. 6 have been "normalized", therefore, to minimize this discrepancy. Figure 6 (a) reveals that solutions of butyl alcohol in hexyl alcohol effectively reproduce the maximum in $\dot{D}(200)$ found in pentyl alcohol and shown in Fig. 5. Similarly, Fig. 6 (b) reveals that solutions of nonyl alcohol in heptyl alcohol reproduce the maximum in drilling efficiency noted in octyl alcohol.
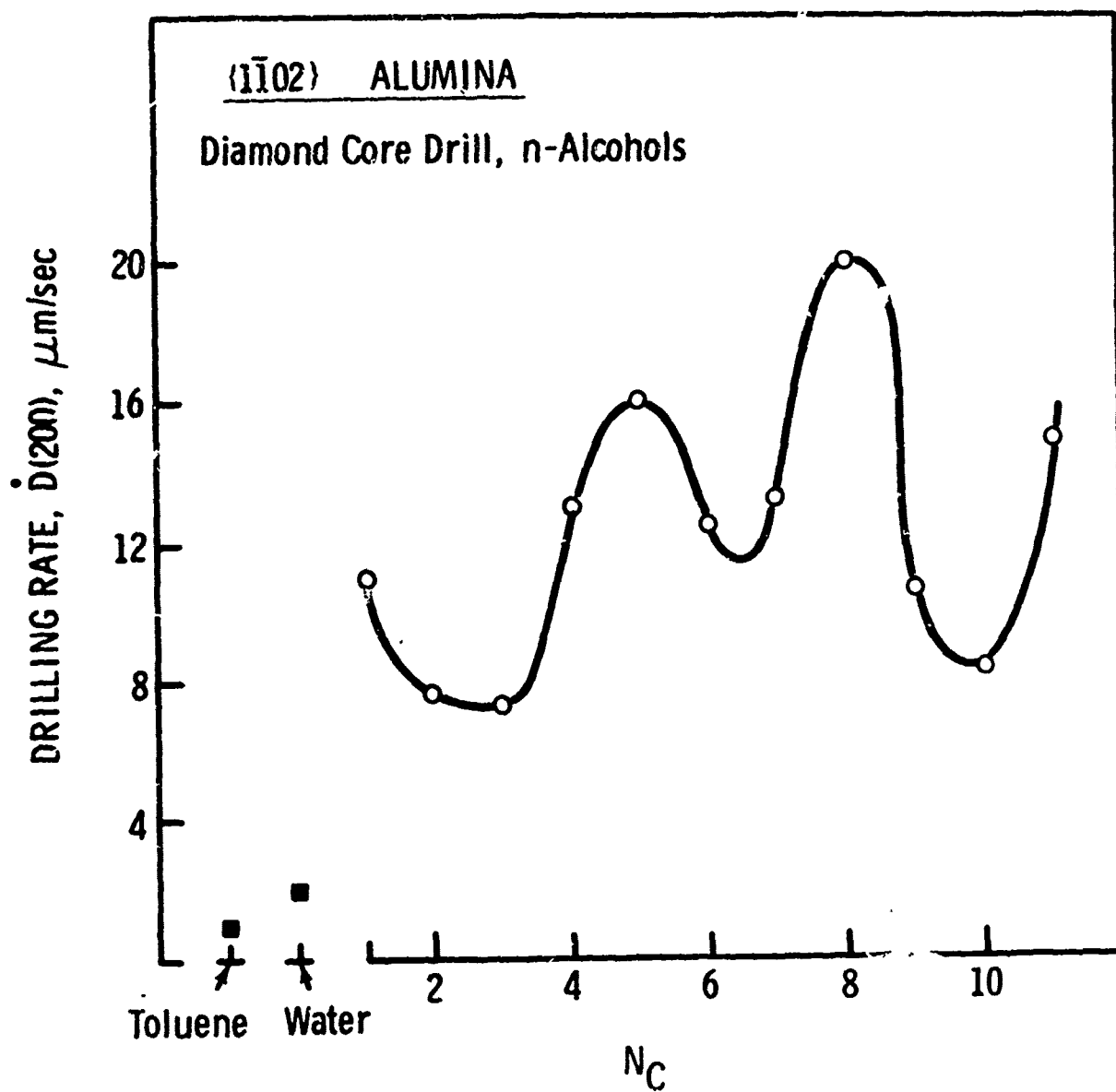
Fig. 5 - Rate of drilling of alumina mono-crystals in the n-alcohols, toluene and water.
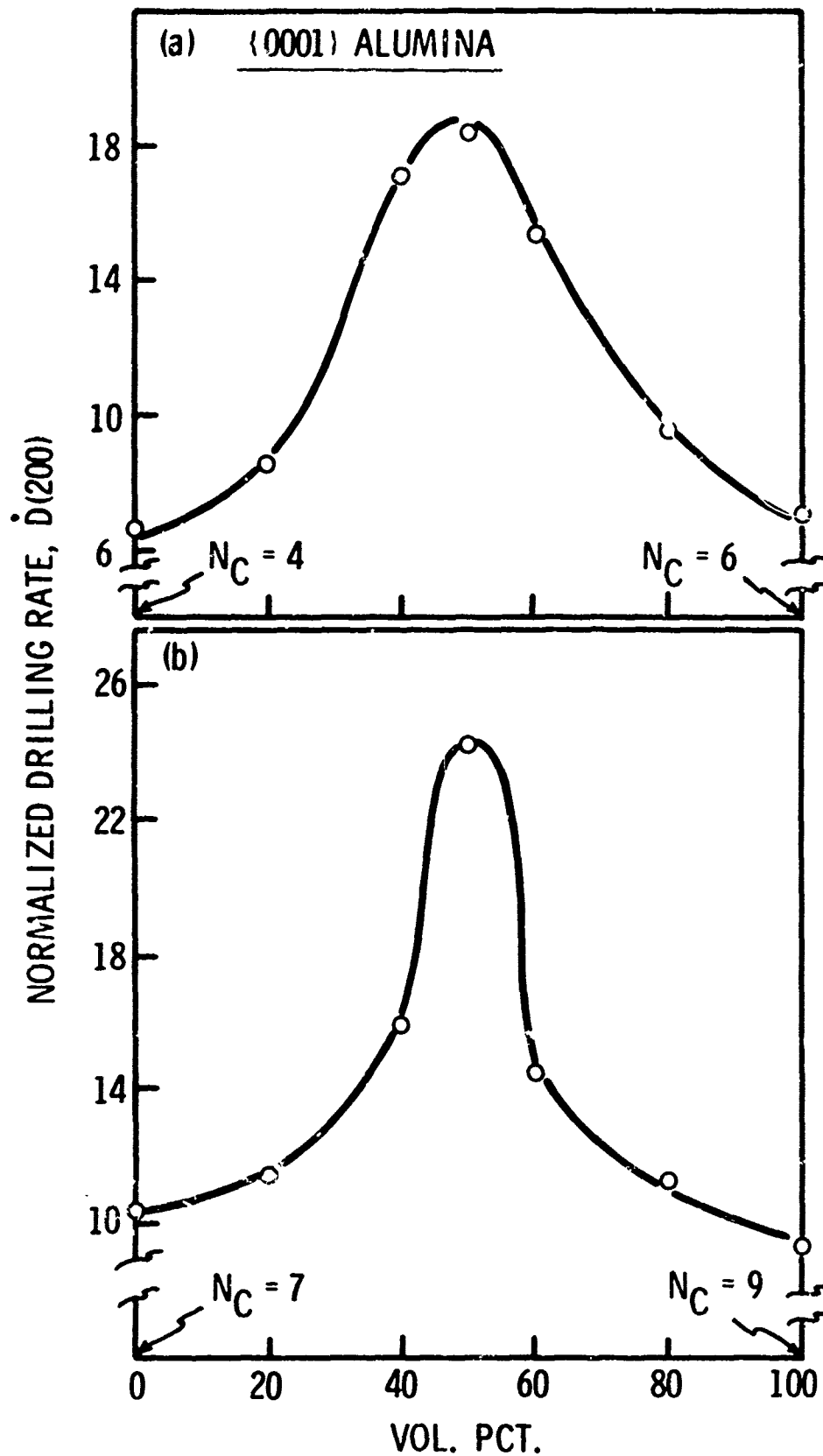
Fig. 6 - Rate of drilling of alumina mono-crystals in binary solutions of the n-alcohols.

Figure 7 presents the drilling data for the Avco alumina, and also some data from a limited number of tests on Lucalox. Both aluminas exhibit the characteristic double maximum in $\dot{D}(200)$. For the Avco material, maxima in $\dot{D}(200)$ occurred in pentyl and decyl alcohols. For the Lucalox material, the first maximum was shifted to hexyl alcohol, but the second again occurred in decyl alcohol. These shifts probably are related to differences in the concentration and distribution of impurities[4]. Of especial interest, however, are the sixfold increase in the drilling rate of the Avco alumina in pentyl alcohol with respect to that in water, and the similar two to threefold increase for Lucalox in hexyl alcohol.

IV. Discussion

This work has confirmed and extended the earlier observation[18] that adsorbed species can markedly influence the near-surface hardness of alumina, and has demonstrated that this effect can be usefully employed to facilitate the machining of both mono- and polycrystalline samples of this material. While the differences in near-surface hardness observed were only of order 25 - 35%, they were responsible, at least in part, for up to tenfold variations in the rates of material removal. Compare, for example, the data for water and octyl alcohol in Fig. 5 . This work has also revealed that a simple relationship exists between the surface charge on alumina, as manifested by its ζ-potential, and its pendulum hardness and machinability. Specifically, alumina is hardest and most readily machined with
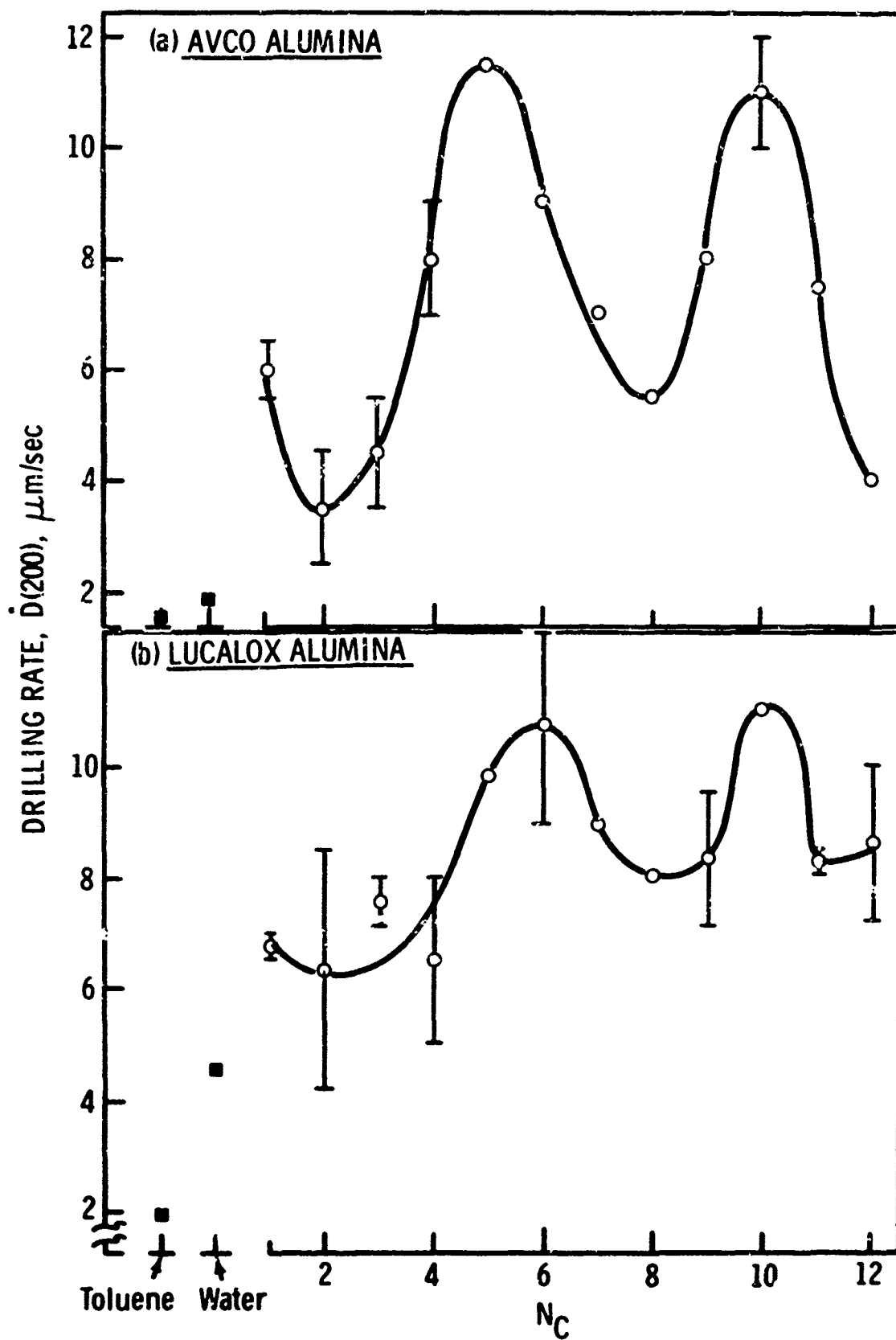
Fig. 7 - Rate of drilling of two polycrystalline aluminas in the n-alcohols, toluene and water.

a diamond core bit at its zero point of charge. This observation is contrary to what might be expected on the basis of the "reduction in surface free energy" hypothesis for adsorption-dependent mechanical phenomena. On that hypothesis, drilling efficiency should be least at the z.p.c., since this is usually assumed to coincide with the maximum value of surface energy*. The observed correlation is consistent, however, with the view[6,7] that it is the influence of the adsorbate on near-surface flow and flow-dependent fracture behavior which is responsible for chemomechanical effects in the machining of non-metallic solids. In this instance, any environment which softens the surface of alumina (with respect, say, to its hardness at its z.p.c.) will reduce the efficiency of drilling with a diamond core bit, because the cutting energy of the bit will then be dissipated in part by plastic flow instead of being used primarily to create the "brittle" cracks considered to control chip formation. Of course, if a carbide spade bit had been used in these studies -- which proved impractical because of the extreme hardness of alumina -- or if rates of material removal by slow abrasion (wear) had been the parameter studied, then the opposite influence of environment would have been expected, because chip formation in these cases is throught to be dominated by plastic shearing processes. Figure 4 suggests that in these instances propyl alcohol (N_C=3) would have been a better cutting environment than pentyl alcohol (N_C=5).

It is also interesting to note that, in contrast to the observations of Rebinder and his colleagues [28] on the value of hardness "reducers" in rock drilling, this work has demonstrated the

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*In reality it is the surface stress that is a maximum at the z.p.c., and for solids this is not necessarily equal to the surface energy.[27]

beneficial effects of hardness "enhancers". In practice, of course, the most effective cutting environment will depend on the cutting action of the bit, i. e., on the mechanisms of chip formation.

Unfortunately, the correlation between ζ-potential and pendulum hardness shown in Figs. 4 (a) and 4 (b) is not as convincing as might be desired, because the pendulum hardness minimum shown by alumina in propyl alcohol is not reflected by a maximum in the ζ-potential data of Gortner as plotted in Fig. 4 (a), and because the suggested variation of ζ-potential with N_C when $N_C > 7$ is speculative. However, Taylor's preliminary data indicate that the ζ-potential is approximately zero when $N_C = 8$ and that, contrary to Gortner's results, it does exhibit a maximum in propyl alcohol. Such a maximum at $N_C = 3$ seems intuitively reasonable, since the ζ-potential of alumina is positive in water ($N_C = 0$), negative in methyl alcohol ($N_C = 1$), and zero when N_C is somewhere between 4 and 6.

The correlation observed between pendulum hardness and ζ-potential suggests a simple explanation for the drilling behavior observed in binary solutions of alcohols. Presumably, when an alcohol which produces a negative charge on the surface of alumina (e. g., butyl alcohol, $N_C = 4$) is added in various proportions to one which produces a positive charge (e. g., hexyl alcohol, $N_C = 6$), there is some composition which will produce an effective surface charge of zero. In this solution the pendulum hardness of the alumina will be a maximum. If correct, this interpretation has a most important implication, namely that the specific feature of pentyl alcohol which causes it to be such a good

cutting environment for a diamond core bit is that it produces approximately zero charge on the surface of alumina. Hence, any environment which produces the same surface charge under the same dynamic conditions of drilling should give similar increases in drilling efficiency, with only minor variations due to the lesser influences of the lubricant or coolant properties of the cutting environment. The way appears clear, therefore, for the logical development of economic, biodegradable and non-toxic cutting fluids for alumina. The observation that relatively pure polycrystalline aluminas exhibit an environment-sensitivity of drilling behavior very similar to that of monocrystals (cf. Figs. 5, 7 (a) and 7 (b)), is most encouraging in this regard.

At this time, no detailed mechanistic interpretation of the effects described is possible for two reasons. First, because little is known about the chemisorption of the n-alcohols on alumina, and how this is influenced by alcohol chain length, crystal orientation, or the type, concentration and distribution of impurities in the solid; and second, because of our lack of knowledge regarding the electronic structure of the crystal surface and of the point defects and dislocation cores in the near-surface region. It seems reasonable to suggest, however, that the present effects arise in much the same way as do chemomechanical effects in MgO and CaF_2[3-5], namely that the electron transfer processes involved in chemisorption influence both the state of ionization of near-surface point defects and impurities, and also the charges on near-surface dislocations. As a consequence, the interactions between dislocations, the lattice, and the point defect structure of the crystal

(which determine dislocation mobility) are changed. Accordingly,
hardness, which is a measure of dislocation mobility, also is influenced.

Clearly, much work will be required before the specific
mechanisms involved are likely to be understood in any greater detail.
However, exploitation of these effects need not await this eventuality.
Given awareness of the empirical relationship between ζ-potential
and near-surface hardness, and recognition of the need to take into account
the intended mode of cutting (i.e., mechanism of chip formation), signi-
ficant improvements over current rates of material removal (or, conversely,
reductions in current rates of wear) should be possible for alumina,
merely by the use of an appropriate liquid environment. In theory,
the development of superior, economical, water-based cutting environ-
ments, incorporating appropriate and carefully controlled amounts of
surface-charge determining species (e.g., anionic or cationic sur-
factants) should be readily accomplished. This is one of the objectives
of our continuing program.

Acknowledgements

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